

Magnetic long-range order induced by quantum relaxation in single-molecule magnets

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Can magnetic interactions between single-molecule magnets (SMMs) in a crystal establish long-range magnetic order at low temperatures deep in the quantum regime, where the only electron spin-fluctuations are due to incoherent magnetic quantum tunneling (MQT)? Put inversely: can MQT provide the temperature dependent fluctuations needed to destroy the ordered state above some finite T_c , although it should basically itself be a T -independent process? Our experiments on two novel Mn_4 SMMs provide a positive answer to the above, showing at the same time that MQT in the SMMs has to involve spin-lattice coupling at a relaxation rate equaling that predicted and observed recently for nuclear spin-mediated quantum relaxation.

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Despite the large number of studies on magnetic quantum tunneling (MQT) in molecular crystals of single-molecule magnets (SMMs) [1], the question whether it is able to bring the spin system into thermal equilibrium with the lattice, remains unsolved. Prokof'ev and Stamp [2] have suggested that interaction with rapidly fluctuating hyperfine fields can bring a significant number of electron spins into resonance. Coupling to a nuclear spin bath indeed allows ground-state tunneling over a range of local bias fields ξ much larger than the tunnel splitting Δ , whereas, in its absence, tunneling would happen only if ξ is $\sim \Delta$ or less. Within this theory, magnetic relaxation could thus in principle occur with no exchange of energy with the phonons of the molecular crystal [3]. Support for the Prokof'ev/Stamp model came from magnetic relaxation studies on the Fe_8 SMM [4]. However, these experiments covered only initial stages of the relaxation process, leaving open the question whether the final state corresponds to a thermal equilibrium. When MQT is combined with coupling to a heat bath, dipolar couplings between cluster spins can induce long-range magnetic ordering (LRMO) at sufficiently low temperatures [5]. This phenomenon has not been observed yet for any of the known SMMs relaxing by MQT. Attempts have been made in Fe_8 and Mn_{12} in particular, by increasing the tunneling rate by means of an applied transverse field [6]. However, the failure is inherent to the approach, since the applied fields needed are much higher than the weak interaction energies involved, and will thus destroy the LRMO.

In this letter, we present zero-field time-dependent specific heat measurements performed on two novel tetranuclear molecular clusters, both with net cluster spin $S = 9/2$, denoted by Mn_4Cl and Mn_4Me , which have similar cluster cores but different ligand molecules. For both, the cluster spins become blocked along their anisotropy axes for temperatures in the liquid helium range, and relax-

ation below ~ 0.8 K can thus only proceed by incoherent MQT between the two lowest lying states $m = \pm S$. For both compounds we prove below that the MQT has to be inelastic. For Mn_4Me , the tunneling rates are found sufficiently high to establish, even at zero field, thermal equilibrium conditions down to the lowest temperatures (~ 0.1 K). Accordingly, the MQT channel enables the occurrence of LRMO between the cluster spins at $T_c = 0.21$ K. Comparing the magnitude of T_c with Monte Carlo simulations suggests the coexistence of dipolar and weak superexchange interactions between clusters. In view of the essential role of the dynamic nuclear bias in the MQT mechanism, our results call for an extension of the nuclear-spin mediated quantum relaxation model [2] to include inelastic processes, where MQT is accompanied by phonon creation or annihilation.

Analytically pure samples of the compounds $\text{Mn}_4\text{O}_3\text{L}(\text{dbm})_3$, with $\text{L} = \text{Cl}(\text{OAc})_3$ or $[\text{O}_2\text{C}(\text{C}_6\text{H}_4\text{-}p\text{-Me})_4]$, hereafter abbreviated as Mn_4Cl and Mn_4Me , were prepared as described in Ref. [7]. All samples were characterized by elemental analysis. Both molecules possess a distorted cubane core with one Mn^{4+} ion (spin $S = 3/2$) and three Mn^{3+} ions ($S = 2$), superexchange coupled via three oxygen ions. The *intra*-cluster exchange couplings have been studied by magnetic susceptibility measurements [7]. Below $T \lesssim 10$ K, the four Mn spins become ordered with a net total spin $S = 9/2$ subject to an uniaxial crystal field [8], the symmetry axis running approximately through the Mn^{4+} ion and the L-ligand. Whereas Mn_4Cl has a local virtual C_{3v} symmetry, the more bulky carboxylate ligand distorts and lowers the symmetry (C_s) of Mn_4Me in the crystal and increases the magnitude of the uniaxial anisotropy [7, 8].

Low-temperature specific heat measurements were performed by a home-made calorimeter using a thermal relaxation method, see Ref. [6]. By varying the thermal

resistance of the thermal link between calorimeter and cold-sink, the characteristic timescale τ_e of the experiment can be varied. In this way time-dependent specific heat measurements can be exploited to investigate spin-lattice relaxation when the relaxation time becomes of the order of τ_e ($\sim 1 - 100$ s) [9]. The samples consisted of 1 – 3 mg of polycrystalline material, mixed with 2 – 5 mg of Apiezon-N grease to ensure good thermal contact. The high-temperature ($2 \text{ K} < T < 300 \text{ K}$) specific heat was measured for a Mn_4Cl pellet sample of about 40 mg using a commercial (PPMS) calorimeter.

The specific heat C/R of Mn_4Cl is shown in Fig. 1, which combines data obtained for $\tau_e \approx 2$ s, 8 s, and 300 s (as estimated at $T = 0.4 \text{ K}$) with the ones obtained with the high- T calorimeter. Let us first consider data measured for $T > 1 \text{ K}$, where C is independent of τ_e . A λ -type anomaly is observed at $T \simeq 7 \text{ K}$, having a relative height of $2.5 R$. Measurements with an applied magnetic field (not presented here) have shown that this anomaly is insensitive to the field, proving that it has to be associated to a structural phase transition. Between 1 K and 7 K, C is dominated by contributions from the lattice phonons and from transitions between energy levels of the $S = 9/2$ multiplet split by the crystal field.

Neglecting, in first approximation, the Zeeman splittings ξ due to effective fields representing the hyperfine interaction and the *inter*-cluster magnetic couplings, the spectrum of energy levels is doubly degenerate at zero-applied-field, so that C only depends on transitions between levels inside each of the potential wells that are separated by the anisotropy energy barrier U . We shall call this the *intra*-well contribution. The associated multilevel Schottky anomaly is calculated with the eigenvalues of the spin Hamiltonian

$$\mathcal{H} = -DS_z^2 - E(S_x^2 - S_y^2) + A_4S_z^4 \quad (1)$$

with parameters D , E and A_4 obtained independently from inelastic neutron scattering and high-frequency EPR measurements [10, 11]. The *intra*-well specific heat decreases exponentially as T decreases and, since the first excited $m = \pm 7/2$ level is about $(2S - 1)D = 5.5 \text{ K}$ above the $m = \pm 9/2$ ground-state doublet, it becomes almost negligible when $T \leq 0.8 \text{ K}$ (Fig. 1). Adding the lattice contribution, calculated with a Debye temperature $\theta_D \simeq 15 \text{ K}$, to the Schottky accounts well for the experimental data (solid line in Fig. 1). The lattice specific heat above 10 K appears to be composed of a number of Einstein-type contributions (not shown).

Below 1 K, we expect the equilibrium magnetic specific heat (C_m) to be dominated by two contributions. The first arises from incoherent MQT events inside the ground-state doublet that is split by the action of the effective fields arising from hyperfine interactions and *inter*-cluster dipolar coupling. The second is the specific heat C_{nucl} of the nuclear spins of Mn, whose energy levels are split by the hyperfine interaction with the atomic

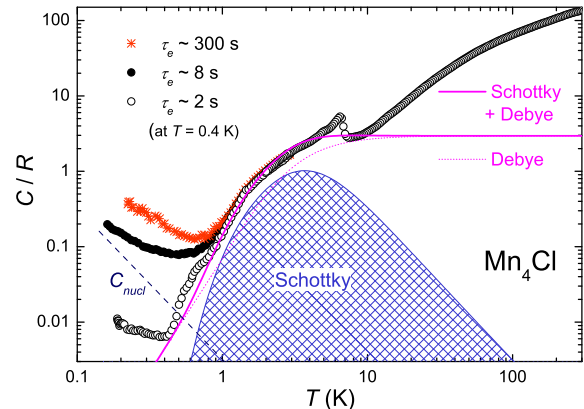


FIG. 1: Temperature dependence of the specific heat of Mn_4Cl measured for $\tau_e \approx 2$ s, 8 s and 300 s. Solid line, sum of the Debye term of the lattice (dotted line) plus the Schottky contributions; dashed line, calculated nuclear contribution C_{nucl} .

electron spins. The dashed line in Fig. 1 represents C_{nucl} calculated with the hyperfine constants $A_{hf} = 7.6 \text{ mK}$ and $A_{hf} = 11.4 \text{ mK}$ for, resp., Mn^{3+} and Mn^{4+} ions, obtained from ESR [12]. Experiments performed for the longest $\tau_e \approx 300$ s show indeed a large low- T contribution. By contrast, the specific heat decreases by almost two orders of magnitude when $\tau_e \approx 2$ s, evidencing that τ_e has a large effect in this temperature range. This shows that the equilibrium between the relative populations of the $+9/2$ and $-9/2$ states cannot be established within τ_e if this is too short. We note that, for the shortest τ_e , the low- T specific heat becomes even smaller than C_{nucl} , indicating that both nuclear and electron spins are out of equilibrium. This is understandable, since the only channel for the nuclear spins to exchange energy with the lattice is via the electron spins. The strong connection between nuclear and electron spin-lattice relaxation has earlier been observed for Mn_{12} , Mn_6 and Fe_8 [6, 13].

The experimental C/R of Mn_4Me , measured for $\tau_e \approx 4$ s (as estimated at $T = 0.4 \text{ K}$), is shown in Fig. 2 together with the calculated contributions of the lattice and the nuclear spins, and the *intra*-well Schottky contribution. The experimental data display a λ -anomaly at $T_c = 0.21 \text{ K}$ that we attribute to the onset of LRMO. The Schottky anomaly is calculated as for Mn_4Cl with parameters obtained from high-frequency EPR [10, 11]. For $T > 1 \text{ K}$, the remaining contribution is given by the lattice and is well described by the sum of a Debye term for the acoustic low-energy modes plus an Einstein term for a higher energy mode, with values $\theta_D \simeq 12.3 \text{ K}$ and $\theta_E \simeq 22 \text{ K}$ for, resp., the Debye and Einstein temperatures. Below 0.15 K, the specific heat of Mn_4Me shows a clear upturn that can be described by $C_{nucl}/R \simeq 4.27 \times 10^{-3}/T^2$. This contribution is well fitted using hyperfine constants $A_{hf} = 8.7 \text{ mK}$ and

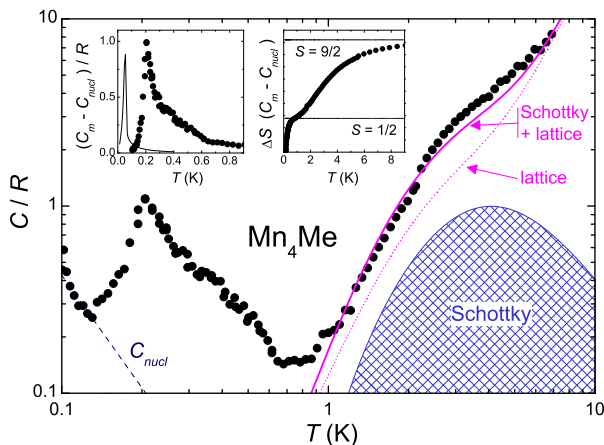


FIG. 2: T -dependent specific heat of Mn_4Me measured for $\tau_e \approx 4$ s. Dashed line, calculated nuclear contribution C_{nuc} ; solid line, sum of lattice (dotted line) plus Schottky contributions. Insets: electronic C_m and entropy variation ΔS , after subtraction of C_{nuc} . Solid line, calculated dipolar ordering for the easy axis along the (110) direction (see text); dashed lines, high- T entropy limits for $S = 1/2$ and $S = 9/2$.

$A_{hf} = 13.8$ mK for, resp., Mn^{3+} and Mn^{4+} ions. These values are of the same order as for Mn_4Cl and are close to those reported by Zeng and Dismukes for a natural Mn_4 cluster [12].

As seen in Fig. 2, the magnetic ordering peak and the calculated Schottky due to the splitting of the $S = 9/2$ multiplet are well separated in temperature. This is confirmed by the analysis of the temperature dependence of the electronic entropy $\Delta S(T) = \int_0^\infty [C_m(T) - C_{\text{nuc}}(T)]/T dT$ (right inset of Fig. 2). As expected, the total entropy of the electron spins tends to $R \ln(2S + 1)$, with $S = 9/2$, at high temperatures. However, for the magnetic ordering region ($T < 0.8$ K), ΔS corresponds to an effective spin $S = 1/2$, as appropriate for a two-level system. This proves that there only the two lowest levels ($m = \pm 9/2$) are populated and contribute to C_m .

We note that, although the anisotropy barrier $U \simeq DS^2 - A_4S^4 - |E|S^2$ amounts to ≈ 14 K for both Mn_4Me and Mn_4Cl , due to the lower symmetry of Mn_4Me the 2nd-order off-diagonal term (E) in the Hamiltonian of Eq. (1), and thus also Δ of the ground-state, will be much larger for this compound. This is confirmed by high-frequency EPR experiments that give $E/D \simeq 0.21$, i.e., nearly 5 times larger than for Mn_4Cl [10, 11]. We observe that this difference has a very large influence on the spin-lattice relaxation. For similar τ_e values, the electron spins of the Mn_4Cl molecule go off equilibrium below $T = 0.8$ K (Fig. 1), whereas for Mn_4Me we observe thermal equilibrium for electron and nuclear spins down to the lowest temperature. We conclude this from the fact that (i) the total electronic entropy contribution equals the expected limit for $S = 9/2$; (ii) the remaining specific heat below 0.15 K agrees well with the calculated C_{nuc} .

As commonly found in molecular clusters, the magnetic core of Mn_4Me is surrounded by a shell of non-magnetic ligand molecules. It follows that, *inter*-cluster superexchange interactions are very weak, leaving the *inter*-cluster dipolar coupling responsible for magnetic ordering [13]. To check this for Mn_4Me , we have performed Monte Carlo simulations, as described in Ref. [5], for a $S = 9/2$ Ising model of magnetic dipoles regularly arranged on the Mn_4Me lattice. We have repeated our calculations for several orientations of the molecular easy axis (an example is given in the left inset of Fig. 2 for the easy axis along the (110) direction). The calculated T_c 's are always much smaller than the experimental value. Consequently, the Mn_4Me molecules are also coupled by weak superexchange interactions. Indeed, by adding an *inter*-cluster nearest-neighbor exchange interaction $|J|/k_B \simeq 0.14$ K to our dipolar calculations, we reproduce the experimental T_c value [14].

In order to estimate the spin-lattice relaxation rate Γ for Mn_4Cl at low temperatures, we have used the relation for the time-dependent specific heat $C_m(t) = C_0 + (C_{eq} - C_0) [1 - e^{-\Gamma \tau_e}]$, where C_0 and C_{eq} are the adiabatic and equilibrium limits of the specific heat, respectively [9]. For the electron spins, C_0 is to good approximation given by the *intra*-well Schottky specific heat, whereas the “slow” specific heat at equilibrium corresponds to excitations involving transitions between the two wells. We have fitted, thus, the $C_m(\tau_e)$ data of Mn_4Cl , taking at each temperature for C_{eq} the $C_m(T)$ measured for Mn_4Me (in the range $T > T_c$). We show $\Gamma(T)$ in Fig. 3, together with data from ac-susceptibility and (short-time) magnetic relaxation experiments [15]. For $T > 1.7$ K, Γ follows the Arrhenius law, with $U \simeq 13.5$ K and $\tau_0 \approx 1.4 \times 10^{-7}$ s. For $T \lesssim 0.8$ K, Γ deviates from this thermal-activation law, in remarkable agreement with the magnetic relaxation data. Its weak temperature dependence confirms that relaxation to thermal equilibrium is dominated by direct MQT transitions within the ground-state doublet.

Summing up, we have proven that for both compounds thermal contact between spins and lattice is established by MQT fluctuations. For Mn_4Me , the associated rate is even fast enough to produce thermal equilibrium down to the lowest temperature and thus enable LRMO. This implies $\Gamma \gtrsim 1/\tau_e \simeq 1$ s $^{-1}$. For Mn_4Cl , we find a lower rate ($10^{-1} - 10^{-3}$ s $^{-1}$) for $T \lesssim 0.8$ K. It is of interest to compare the experimental Γ for Mn_4Cl with predictions from conventional models for spin-lattice relaxation, assuming that the $m = \pm 9/2$ energy levels of the cluster spins are time-independent. We have simulated the effect of *inter*-cluster dipolar coupling and hyperfine interactions by introducing static magnetic fields $B_x = 150$ G and $B_z = 350$ G [16]. The presence of these Zeeman terms is essential, otherwise tunneling would be forbidden for half-integer spin $S = 9/2$ [17]. We calculated Γ by solving a master equation, including *intra*- as well as

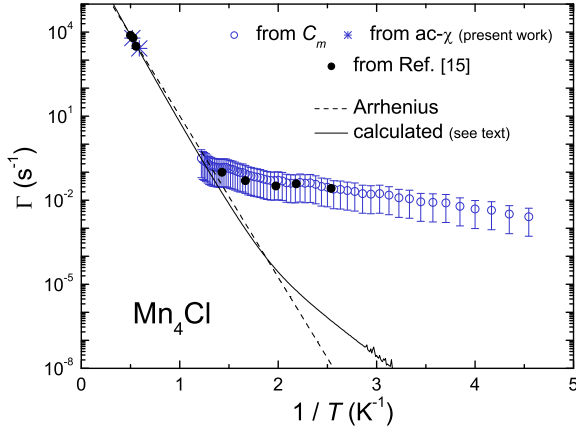


FIG. 3: Spin-lattice relaxation rate of Mn_4Cl : (*) and (●) [15] obtained from ac-susceptibility and magnetic relaxation data; (○) obtained by fitting the $C_m(\tau_e)$ data of Fig. 1 (see text). Dashed line is fit of high- T data to Arrhenius law; solid line is calculated for magnetic fields $B_x = 150$ G and $B_z = 350$ G (see text).

inter-well transitions, induced by phonons only, between exact eigenstates of the spin Hamiltonian of Eq. (1), as discussed in Ref. [9] and recently applied to the analysis of C_m of Fe_8 and Mn_{12} clusters [6]. The result (solid line in Fig. 3) agrees well with the activated behavior observed at high- T , but fails to account for Γ measured below 1 K by six orders of magnitude! This large discrepancy can not be ascribed to errors in the estimated elastic properties of the lattice. Both the pre-factor of the Arrhenius law and the measured value of θ_D give a value of $c_s \simeq 5(1) \times 10^2$ m/s for the speed of sound. By contrast, Γ observed at low- T would require c_s and θ_D to be 15 times smaller. This would give rise to a large lattice specific heat well below 1 K, which is not observed.

It appears therefore that extension to *dynamic* hyperfine fields acting on the cluster-spin levels, as proposed in Ref. [2], is indeed a necessary prerequisite for any model for the MQT of SMMs. Such dynamic bias fields will sweep the tunneling levels with respect to one another, thereby enabling incoherent Landau-Zener type tunneling events. The model predicts quantum relaxation rates agreeing with experiments [4], but so far the relaxation of the cluster spins was thought to occur solely/primarily to the nuclear spin bath, relaxation to phonons was only expected at much longer time-scales. Our specific heat experiments, in which obviously the heat is transferred to the spins *via* the lattice, clearly demonstrate that in fact spin-lattice relaxation *has to be* involved and at much the same fast rates! Since application of ‘conventional’ models for spin-lattice relaxation leads to rates orders of magnitude too low, our data call for an extension of the Prokof’ev/Stamp model in which nuclear spin-mediated

MQT events are combined with creation or annihilation of phonons.

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